

# Photocatalytic activity of $\text{TiO}_2/\text{ZSM-5}$ composites in the presence of $\text{SO}_4^{2-}$ ion

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## Abstract

$\text{TiO}_2/\text{ZSM-5}$  composites were prepared from  $\text{SiO}_2$  of rice husk ash and  $\text{TiO}_2$  sol from hydrolyzed  $\text{TiOSO}_4$  salt. The combined effect of these two materials greatly enhanced the photocatalytic decolorization of methylene blue dye solution. The instant decolorization of the dye solution in the dark by the composite,  $\text{TiO}_2/\text{ZSM-5}$  (wt ratio 1:1), resulted from the combination of the adsorption by ZSM-5 zeolite and  $\text{TiO}_2$  nano-particles, and of  $\text{Na}_2\text{SO}_4$  salt adhering to the composite surface. As a strong flocculating agent, the  $\text{SO}_4^{2-}$  ion caused the precipitation of the dye onto the composite surface which consequently enhanced the photocatalytic decolorization of the dye under UV irradiation. The composite,  $\text{TiO}_2/\text{ZSM-5}$  (wt ratio 1:5), completely decolorized the methylene blue dye in 2.5 h, giving an equivalent performance to that of  $\text{TiO}_2$ , P-25 powder.

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## 1. Introduction

Recently, nanocomposites have been a popular research topic. The composites of nano- $\text{TiO}_2$  and porous material supports with large surface area have received much attention because of their adsorption-supported photocatalytic properties. The potential applications are wastewater treatment and use as antimicrobial agents. The objectives of this research were to study  $\text{SO}_4^{2-}$ -containing  $\text{TiO}_2$  powder and a composite,  $\text{TiO}_2/\text{ZSM-5}$  (wt ratio 1:20 to 1:1), with the expectation that the synergy of  $\text{SO}_4^{2-}$  ion and ZSM-5 would help in solving some handicaps in the practical application of the  $\text{TiO}_2$  photocatalyst. These drawbacks include the surface interaction between the catalyst and guest particles, UV irradiation dependence and difficulty in removal of the spent catalyst. Although there have been a number of like research articles [1–3], none of them have involved a composite containing this much  $\text{TiO}_2$  and  $\text{SO}_4^{2-}$ . In this study, we hydrothermally synthesized ZSM-5 using  $\text{SiO}_2$  from the local rice husk ash (calcined at 700 °C) at 150 °C under autogenous water vapor pressure [4]. The photocatalytic activities of the obtained products were evaluated through the

degradation of the cationic dye, methylene blue (MB), in the presence of  $\text{SO}_4^{2-}$  ion. The results were compared with the commercial  $\text{TiO}_2$  powders, P-25 and ST-01. Photodegradation process was reported to most probably degrade and oxidize various dyes and mixed dye to non-toxic and safer end products such as  $\text{H}_2\text{O}$ , CO,  $\text{CO}_2$  and mineral acids proceeding via a number of intermediate compounds (peroxylated or hydroxylated intermediates) [5].

## 2. Materials and method

### 2.1. Material characterization

ZSM-5, Na based zeolite, was used as the porous support for the synthesized  $\text{TiO}_2$  powder.  $\text{TiOSO}_4 \cdot n\text{H}_2\text{O}$  (Riedel-de Haën), NaOH (AR grade, Merck) and methylene blue (Fluka) were used as source of  $\text{TiO}_2$  sol, pH regulator and degradable dye, respectively. P-25 was from Degussa (Germany) and ST-01 was from Ishihara Sangyo Kaisha (Japan). The obtained  $\text{TiO}_2$  powder, ZSM-5 and the composite were characterized for phase analysis, specific surface area and morphology by XRD (Bruker, D8 Advance), BET (Coulter SA 3100) and SEM (JEOL JSM 6400), respectively. The photocatalytic activity was evaluated by measuring the absorbance in the oxidation of MB dye (using 0.01 g catalyst in 20 ml of

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Table 1  
BET surface area, apparent rate constant and content of adsorbed Na<sub>2</sub>SO<sub>4</sub> of TiO<sub>2</sub>, ZSM-5 and TiO<sub>2</sub>/ZSM-5 composite

Sample, preparation condition (crystal size)	BET surface area (m <sup>2</sup> /g)	<i>k</i> (×10 <sup>−2</sup> h <sup>−1</sup> )	Na <sub>2</sub> SO <sub>4</sub> (g/g powder or composite)
P-25 anatase/rutile [2]	50	224	–
ST-01 anatase [9]	300	105	–
TiO <sub>2</sub> -1, 400 °C, filtered (5 nm, XRD) <sup>a</sup>	73	173	0.4780
TiO <sub>2</sub> -2, 400 °C, washed with 50 ml distilled water (5.4 nm, XRD)	96	71	n.d.
TiO <sub>2</sub> -3, 400 °C, sulfate-free (5.8 nm, XRD)	123	25	n.d.
TiO <sub>2</sub> -4, 500 °C, filtered (8.2 nm, XRD)	40	193	n.d.
TiO <sub>2</sub> -5, 700 °C, filtered (27 nm, XRD)	24	243	n.d.
ZSM-5 (5 μm, SEM)	306	–	–
TiO <sub>2</sub> /ZSM-5 = 1:20	306	41	0.0530
TiO <sub>2</sub> /ZSM-5 = 1:10	294	73	0.0939
TiO <sub>2</sub> /ZSM-5 = 1:5	260	111	0.1775
TiO <sub>2</sub> /ZSM-5 = 1:2.5	247	19	0.2117
TiO <sub>2</sub> /ZSM-5 = 1:1	212	–	0.3885

n.d. = not determined. It is understood that all the samples contain Na<sub>2</sub>SO<sub>4</sub>, except TiO<sub>2</sub>-3, and it is assumed that TiO<sub>2</sub>-1, TiO<sub>2</sub>-4 and TiO<sub>2</sub>-5 contain the same amount of Na<sub>2</sub>SO<sub>4</sub> but there is lesser amount in TiO<sub>2</sub>-2.

<sup>a</sup> TiO<sub>2</sub>-1 was employed in the preparation of all the composites due to its large surface area and residual SO<sub>4</sub><sup>2−</sup> content.

0.02 mM aqueous dye solution with continuous stirring) at 664 nm under 4 h UV irradiation (intensity 2 mW/cm<sup>2</sup>, using 10 W black light at 300–400 nm), using a UV–vis spectrophotometer (PerkinElmer Lambda 35). The experiment was performed at pH 5.8 which was the natural pH of the MB dye solution. Referring to the previous literature, a wide range of isoelectric point (IEP, pH 4–6) for TiO<sub>2</sub> [6] had been suggested and the point of zero charge (ZPC) for TiO<sub>2</sub> in the presence of electrolyte, SO<sub>4</sub><sup>2−</sup>, had been reported to be at pH 6.6 and due to the adsorbed SO<sub>4</sub><sup>2−</sup>, the surface of SO<sub>4</sub><sup>2−</sup>-containing TiO<sub>2</sub> should be less positive [7]. For accuracy, the values of zeta potential of ZSM-5 and the obtained SO<sub>4</sub><sup>2−</sup>-containing TiO<sub>2</sub> in aqueous solution were determined by zetasizer (Malvern, Nano ZS) at pH 5.8. It was found to be −7 mV for TiO<sub>2</sub> and −17 mV for ZSM-5, hence explaining the adsorption of the cationic MB dye. The content of SO<sub>4</sub><sup>2−</sup> ion in the TiO<sub>2</sub> powder was taken via the weight of BaSO<sub>4</sub> precipitates (calcined at 900 °C) in the washed solution.

## 2.2. Method

The SO<sub>4</sub><sup>2−</sup>-containing TiO<sub>2</sub> sol (SO<sub>4</sub><sup>2−</sup>/TiO<sub>2</sub> sol) of pH 6 (adjusted by NaOH) was prepared from TiOSO<sub>4</sub> salt, using the method described by Sakthivel et al. [8] and the preparation of TiO<sub>2</sub>/ZSM-5 composite is presented as a flow chart in Fig. 1.

## 3. Results and discussion

### 3.1. Characterization of the products

The values of specific surface area, rate constant for photocatalytic degradation and the content of Na<sub>2</sub>SO<sub>4</sub> remaining on the calcined TiO<sub>2</sub> and the composite are presented in Table 1.

The rate constant of photocatalytic degradation was calculated up to a period of 2 h irradiation using the following equation [10]:

$$\ln \frac{C_0}{C_t} = kt$$

where *C*<sub>0</sub> and *C*<sub>*t*</sub> represent the initial concentration of MB aqueous solution and the concentration measured at the irradiation time, *t*, respectively, and *k* represents the apparent rate constant.

The average crystal size of the powder was calculated from the full width at half maximum of anatase (1 0 1) in the XRD pattern (JCPDS No. 89-4921), using Scherrer's equation [11].

The result of phase analysis by XRD in Fig. 2 clearly revealed the poor crystalline anatase of TiO<sub>2</sub>-1 powder and its coexistence in the composites. The FT-IR spectrum of TiO<sub>2</sub>-1 in Fig. 3 shows an absorption peak of chemisorbed SO<sub>4</sub><sup>2−</sup> at 1131 cm<sup>−1</sup> and another large peak of the OH group at 3433 cm<sup>−1</sup>, characteristics of sulfated TiO<sub>2</sub> [12,13]. It should be noted that the content of sulfate salt adsorbed on each sample of TiO<sub>2</sub> powder was too small to be detected by XRD but the white precipitate obtained after evaporating the collected

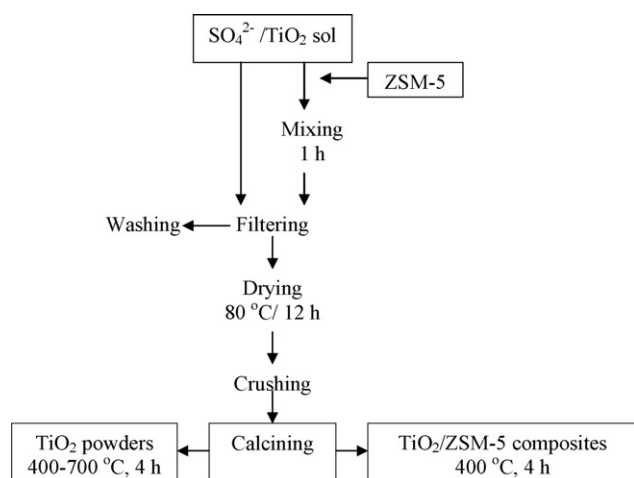


Fig. 1. Flow chart for the preparation of TiO<sub>2</sub>/ZSM-5 composite.

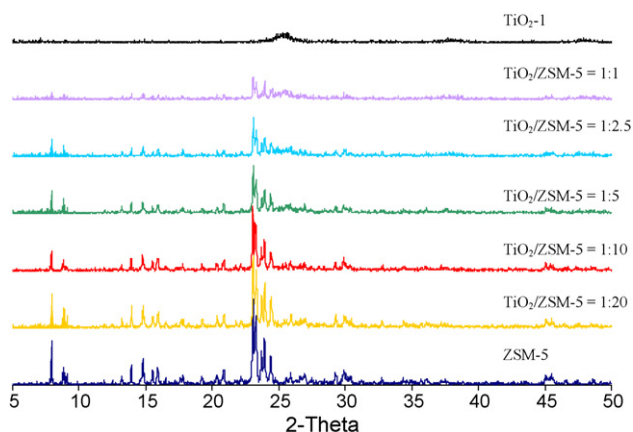


Fig. 2. XRD patterns of ZSM-5,  $\text{TiO}_2$  and  $\text{TiO}_2/\text{ZSM-5}$  composites. (JCPDS No. 42-0023 and 89-4921).

washing waters on a hotplate was detectable by XRD as a mixture of two  $\text{Na}_2\text{SO}_4$  salts (JCPDS No. 37-1465, thernardite (syn) and No. 24-1132,  $\text{Na}_2\text{SO}_4$ ). Therefore, it was reasonable to assume that the excess sulfate ion on  $\text{TiO}_2$  particle was physically adsorbed as  $\text{Na}_2\text{SO}_4$  salt. The SEM micrographs, Fig. 4, shows that the particles of  $\text{TiO}_2$ -1 ( $\sim 5$  nm) only adhered to the surface of ZSM-5 and were not inside the pores ( $\sim 5$  Å).

### 3.2. Photocatalytic results

#### 3.2.1. Photocatalytic activity of $\text{TiO}_2$ powders

The photocatalytic results of the  $\text{TiO}_2$  powders synthesized at various conditions are presented in Fig. 5. The adsorption of dye in the dark of all the powders reached equilibrium at  $\sim 0.5$  h. The absorbance in the dark by  $\text{TiO}_2$ -1 powder was high but under UV irradiation was very low, descending from  $\text{TiO}_2$ -1 to  $\text{TiO}_2$ -5 (crystalline anatase). From the preparation method, it was expected that some amount of  $\text{SO}_4^{2-}$  ion would remain as  $\text{Na}_2\text{SO}_4$  salt (water soluble and mp  $\sim 800^\circ\text{C}$ ) [14] on the surface of  $\text{TiO}_2$  particles. This sulfate salt ionized in the aqueous dye solution producing  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions. Most  $\text{Na}^+$  ions would adsorb onto the weakly, negative charged surface of

$\text{TiO}_2$  and few would diffuse away while the closely diffused  $\text{SO}_4^{2-}$  ions would act as a bridging electrolyte that compressed the double layer of the  $\text{TiO}_2$  sol [15] leading to the flocculation of the  $\text{TiO}_2$  particles with the adsorbed dye in the dark and enhancing the subsequent photocatalysis. The absorbance in the dark of  $\text{TiO}_2$ -2 was approximately the same as  $\text{TiO}_2$ -1 but under UV irradiation was higher. Both absorbances of  $\text{TiO}_2$ -3 (sulfate-free) were the highest. The sequence of absorbance at 0.5 h UV irradiation was  $\text{TiO}_2$ -5 <  $\text{TiO}_2$ -1 <  $\text{TiO}_2$ -4 <  $\text{TiO}_2$ -2 <  $\text{TiO}_2$ -3 and  $\text{TiO}_2$ -5  $\sim$  P-25;  $\text{TiO}_2$ -1,  $\text{TiO}_2$ -4  $\sim$  ST-01. Obviously, the supportive effect of electrolyte on the adsorption mechanism of dye by  $\text{TiO}_2$  powder was confirmed by the low catalytic rate of the washed and  $\text{SO}_4^{2-}$ -free  $\text{TiO}_2$  powders (Table 1).

#### 3.2.2. Photocatalytic activity of $\text{TiO}_2/\text{ZSM-5}$ composites

Since,  $\text{TiOSO}_4$  and  $\text{NaOH}$  were used as the sources of  $\text{TiO}_2$  and the hydrolyzing agent, respectively, it was expected that there would be some trace of  $\text{Na}_2\text{SO}_4$  on the surface of the filtered  $\text{TiO}_2/\text{ZSM-5}$  composite as well as on the  $\text{TiO}_2$  powder after calcining. This expectation was confirmed by the detection of chemically adsorbed  $\text{SO}_4^{2-}$  (Fig. 3). The content of  $\text{Na}_2\text{SO}_4$  adsorbed on  $\text{TiO}_2$ -1 powder was  $\sim 0.478$  g/g powder or composite (Table 1). Those on the composites were dependent on the adsorbed  $\text{TiO}_2$  content. From the results shown in Fig. 6, in the dark, the adsorption of dye by ZSM-5 and composites reached equilibrium at  $\sim 0.5$  h and that of ZSM-5 was nearly the same after UV irradiation. Adsorption limit is characteristic of a particular material and related to its surface area which can be tailored if the material is made into a composite, and in the presence  $\text{Na}_2\text{SO}_4$  the mechanism of adsorption is more complicated. At low  $\text{TiO}_2$  loadings (wt ratio of  $\text{TiO}_2/\text{ZSM-5} = 1:20, 1:10$  and  $1:5$ ), the surface areas of 1:20 and 1:10 composites were not much different from those of the ZSM-5 (Table 1). Therefore the absorbance in the dark was close to that of the ZSM-5, but the photocatalysis under UV irradiation depended on the  $\text{TiO}_2$  content and close contact between the adsorbed dye and  $\text{TiO}_2$  particles, hence the higher  $\text{TiO}_2$  composite showed lower absorbance under UV irradiation. At 1:5  $\text{TiO}_2$  loading, there was an optimal synergy of  $\text{Na}_2\text{SO}_4$  content and surface area of the composite resulting in the highest catalytic rate. On the contrary, at 1:2.5  $\text{TiO}_2$  loading, the surface area of the composite was  $\sim 3/4$  of ZSM-5 and the exposed surface of ZSM-5 was large enough to exhibit the neutralization effect of  $\text{Na}^+$  ion [16]. The composite became less negative, therefore, the dye adsorption in the dark was low, leading to high absorbance and the lowest catalytic rate. From this point and beyond, the content of  $\text{TiO}_2$  was the main factor that controlled the mechanism.

It was noticed that for 1:20 to 1:2.5  $\text{TiO}_2$  loadings, composite particles in the dye solution were in a state of suspension after 0.5 h in the dark and took a few hours to settle. For 1:1  $\text{TiO}_2$  loading, the surface area of the composite was  $\sim 2/3$  of ZSM-5, and the content of ZSM-5 was small (half of ZSM-5) so each composite particle contained quite an amount of  $\text{Na}_2\text{SO}_4$ , hence the flocculating concentration of  $\text{Na}_2\text{SO}_4$  was reached. Consequently, the contacts between  $\text{TiO}_2$  particles

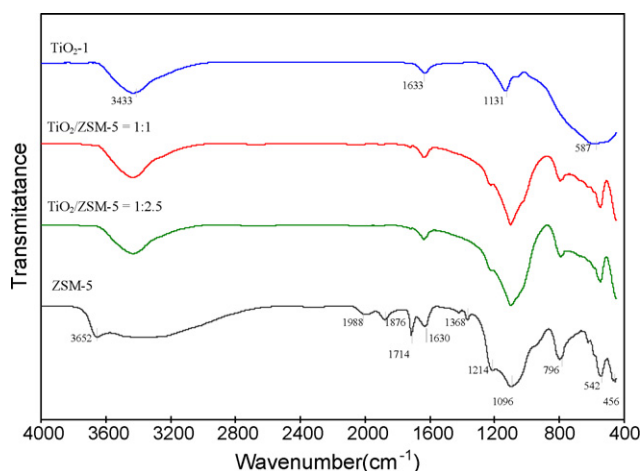


Fig. 3. FT-IR spectra of ZSM-5,  $\text{TiO}_2$  and  $\text{TiO}_2/\text{ZSM-5}$  composites.

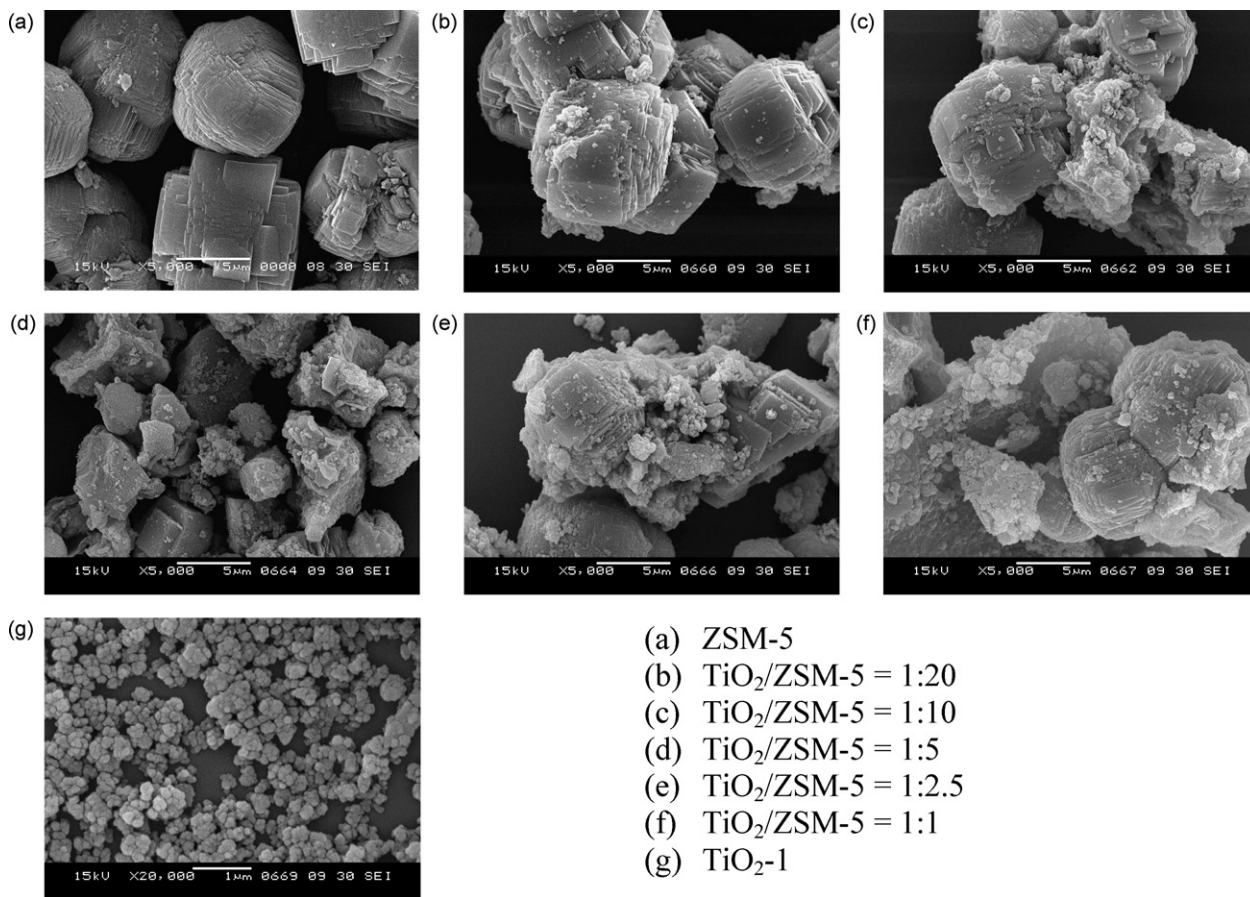


Fig. 4. SEM micrographs of ZSM-5, TiO<sub>2</sub> and TiO<sub>2</sub>/ZSM-5 composites. (a) ZSM-5, (b) TiO<sub>2</sub>/ZSM-5 = 1:20, (c) TiO<sub>2</sub>/ZSM-5 = 1:10, (d) TiO<sub>2</sub>/ZSM-5 = 1:5, (e) TiO<sub>2</sub>/ZSM-5 = 1:2.5, (f) TiO<sub>2</sub>/ZSM-5 = 1:1 and (g) TiO<sub>2</sub>-1.

were enhanced through the powerful flocculation of the ionized Na<sub>2</sub>SO<sub>4</sub> resulting in the forming of loose large flocs of the composite particles. The dye adsorption onto the composite was continuously enhanced by the additional capillary action of the flocs which, on the removal of magnetic stirring, fell down to the bottom of the beaker. Accordingly, all the dye was almost physically adsorbed, and the solution became clear while the settled flocs became deep blue (Fig. 7). The bleaching of the dye solution in the dark was instantaneous and the absorbance dropped to almost zero within 0.5 h. Consequently, the

oxidation of the dye under UV irradiation went on with a gradual change in the absorbance of the dye solution. After 2.5 h, the solutions with 1:5 and 1:1 TiO<sub>2</sub> loadings were colorless and the flocs at the bottom were lighter in color. Fig. 8 is a schematic model proposed for 1:1 TiO<sub>2</sub> loading showing that most of the ionized Na<sup>+</sup> would leave TiO<sub>2</sub> and readily adsorb onto the exposed surface of ZSM-5 because of its stronger negative charged surface leading to neutralization, and an exposed negative charged surface of TiO<sub>2</sub>. It can be said that the mechanism of adsorption of dye in the dark by the

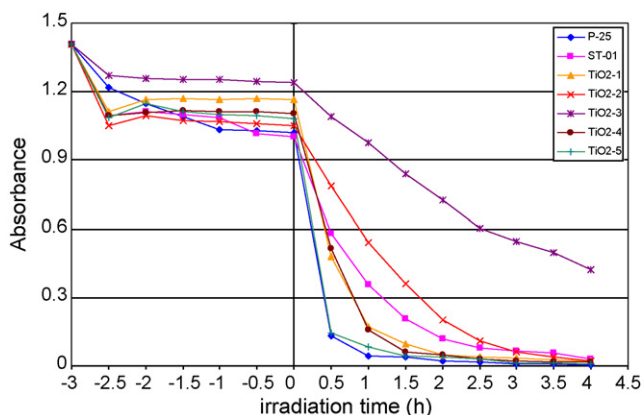


Fig. 5. Photocatalytic results of commercial TiO<sub>2</sub> and synthesized TiO<sub>2</sub>.

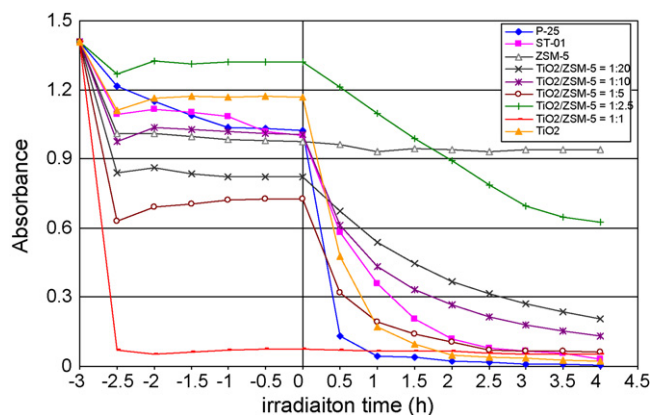


Fig. 6. Photocatalytic activities of TiO<sub>2</sub> powders and TiO<sub>2</sub>/ZSM-5 composites.

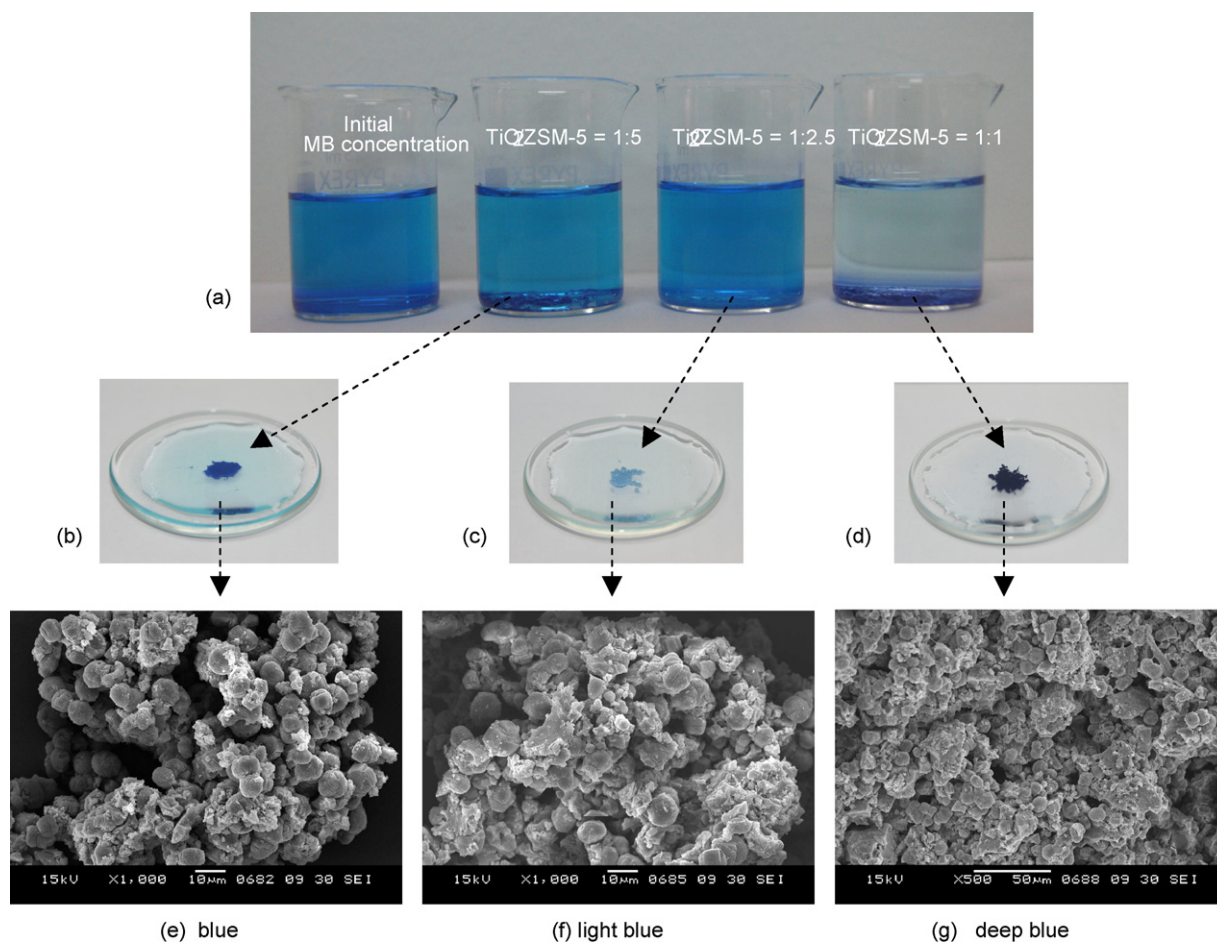


Fig. 7. Photographs of (a) MB adsorption of the composite in the dark and the settled flocs in MB solution containing 0.01 g of (b)  $\text{TiO}_2/\text{ZSM-5} = 1:5$ , (c)  $\text{TiO}_2/\text{ZSM-5} = 1:2.5$ , (d)  $\text{TiO}_2/\text{ZSM-5} = 1:1$  and SEM micrographs ((e), blue in the web version; (f), light blue in the web version; (g), deep blue in the web version) of the settled flocs (air dry) from (b)–(d).

composite was the interaction of both the exposed surface of ZSM-5 and  $\text{TiO}_2$  content. The low absorbance in the dark meant that a high dye content was adsorbed, leading to a better and larger interface contact between the dye and  $\text{TiO}_2$  particles, and hence faster oxidation of the dye under UV irradiation.

Therefore the mechanism of the oxidation of the dye by the composite under UV irradiation directly depended on the weight ratio of  $\text{TiO}_2$  loading. The optimal weight ratio of  $\text{TiO}_2$  loading, taken as the point of optimal interaction between the exposed surface of ZSM-5 and that of  $\text{TiO}_2$ , judging from the

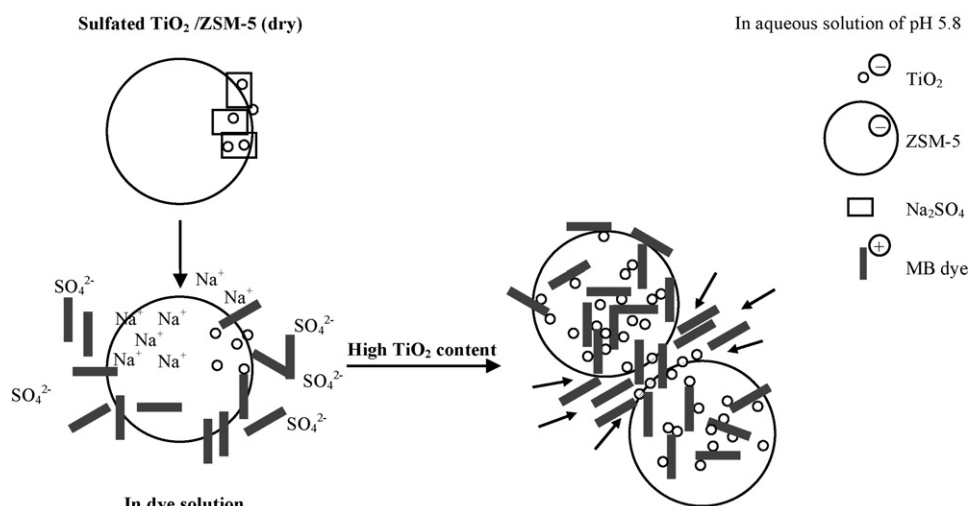


Fig. 8. Schematic model of the interaction.

adsorption in the dark and the catalytic reaction at 0.5 h after UV irradiation was 1:5 TiO<sub>2</sub> loading.

In the case of TiO<sub>2</sub> powders, P-25 and ST-01, it was clear that the mechanisms of adsorption and oxidation of the dye were different from those of the composites. The surface area of the powder accounted for both mechanisms. The better catalytic action of P-25 (50 m<sup>2</sup>/g) over that of ST-01 which has a finer particle size, to a certain extent, may also be supported by its phase composition and slow electron–hole recombination [17]. The ratio of rutile/anatase is about 30/70 in P-25, while ST-01 is 100% large surface area (~300 m<sup>2</sup>/g) anatase. For sample, TiO<sub>2</sub>-1, the photocatalytic action was greatly assisted by the effective content of Na<sub>2</sub>SO<sub>4</sub> electrolyte. However, unlike the case of composites whose particle size was much larger, in TiO<sub>2</sub>-1 powder only small particles of flocs were formed and remained suspended in the solution.

However, besides the sulfate (SO<sub>4</sub><sup>2-</sup>) content and the effect of TiO<sub>2</sub>/ZSM-5 composite, the photocatalytic activities of our TiO<sub>2</sub> powder could also be improved by increasing its crystallinity through higher temperature calcining as seen in Fig. 5. It seemed that the larger particle size or the better crystallinity of TiO<sub>2</sub> enhanced the early catalytic reaction under UV irradiation. However, the rates at 2.5 h of 400–500 °C samples were not much different. The surface area of TiO<sub>2</sub> at 700 °C was 24 m<sup>2</sup>/g (Table 1) and gave the best catalytic reaction with the highest rate at 0.5 h, while the adsorption of dye in the dark was almost the same for all the samples, excluding the SO<sub>4</sub><sup>2-</sup>-free (TiO<sub>2</sub>-3).

#### 4. Conclusion

The SO<sub>4</sub><sup>2-</sup> ion did enhance photocatalytic reaction but there was an optimal content limit. Filtering removed most of the SO<sub>4</sub><sup>2-</sup> salt which would adhere to the TiO<sub>2</sub> surface, and the remaining salt after calcination was the ionizable Na<sub>2</sub>SO<sub>4</sub> which acted as the bridging agent for the TiO<sub>2</sub> sol, promoting flocs which enhanced the physical adsorption through a charge effect of the dye and the subsequent photocatalytic reaction. The combined effect of SO<sub>4</sub><sup>2-</sup> ion and the composite TiO<sub>2</sub>/ZSM-5 was to initiate the large flocs with fast settling and ease of removal leaving a clear supernatant liquid. In summary, the presence of SO<sub>4</sub><sup>2-</sup> ion, the effect of the composite TiO<sub>2</sub>/ZSM-5 and high temperature calcination could improve the photocatalytic reaction of the obtained TiO<sub>2</sub> close to those of P-25 and ST-01. The instantaneous dye adsorption in the dark by sample with high TiO<sub>2</sub> loading, 1:1, was very interesting since

its mechanism was independent of light and the ease of removal of the settled spent flocs could be of good benefit in wastewater treatment. This finding is very interesting in that it can greatly reduce the working time in waste management. The effectiveness of our catalysts owes much to the principles underlying the process of textile dyeing.

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